

Optical Properties of Thin Film Molecular Mixtures

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Introduction

Thin films composed of molecular mixtures of metal and dielectric are being considered for use as solar selective coatings for a variety of space power applications. By controlling the degree of molecular mixing, the solar selective coatings can be tailored to have the combined properties of high solar absorptance, α , and low infrared emittance, ϵ . On orbit, these combined properties would simultaneously maximize the amount of solar energy captured by the coating and minimize the amount of thermal energy radiated. Minisatellites equipped with solar collectors coated with these cermet coatings may utilize the captured heat energy to power a heat engine to generate electricity, or to power a thermal bus that directs heat to remote regions of the spacecraft.

Early work in this area identified the theoretical boundary conditions needed to operate a Carnot cycle in space, including the need for a solar concentrator, a solar selective coating at the heat inlet of the engine, and a radiator.¹ A solar concentrator that can concentrate sunlight by a factor of 100 is ideal. At lower values, the temperature of the solar absorbing surface becomes too low for efficient heat engine operation, and at higher values, cavity type heat receivers become attractive. In designing the solar selective coating, the wavelength region yielding high solar absorptance must be separated from the wavelength region yielding low infrared emittance by establishing a sharp transition in optical properties. In particular, a sharp transition in reflectance is desired in the infrared to achieve the desired optical performance. For a heat engine operating at 450°C, a sharp transition at 1.8 micrometers is desired.² The radiator completes the heat flow through the Carnot cycle.

Additional work has been done supporting the use of molecular mixtures for terrestrial applications.³⁻⁴ Sputter deposition provides a means to apply coatings to the tubes that carry a working fluid at the focus of trough-style collectors. Sputtering offers considerable flexibility in coating conditions, including a wide variety of metal and dielectric targets. Coating designs range from simple two or three layer coatings to complex coatings that are purposely graded to be metal-rich at their base and oxide-rich at their surface in order to yield the desired solar selective properties. In these cermet coatings, molecular islands of metal are thought to be embedded in a three dimensional matrix of dielectric.

Recent work has identified the use of custom made ion beam sputter deposition targets to produce coatings containing molecular mixtures of metal and dielectric.⁵ The targets are cylindrical and the surface consists of a gradually changing composition of metal and dielectric. Rotating the cylinder under the beam during ion beam sputter deposition yields a coating that is a molecular mixture of metal and dielectric, with the composition changing through the thickness of the coating. The optical properties of these coatings are not only dependent on their thickness and chemical composition, but are also dependent on the extent of the through thickness gradient established during deposition.

This paper presents a summary of the optical properties of several thin film molecular mixtures designed as solar selective coatings. Optical performance is first identified as a function of wavelength,

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from the ultraviolet to the visible and infrared. Coating composition, thickness, and gradient from metal to dielectric also play an important role. Additional work for future activities is also identified.

Materials and Methods

The production of the thin film solar selective coatings has been summarized in detail elsewhere.² Briefly, ion beam sputter deposition is used to generate thin film molecular mixtures of metal and dielectric using a cylindrical target having a varying amount of metal and dielectric exposed around its perimeter. Figure 1 shows one of the targets installed in the ion beam sputter deposition facility. At the beginning of

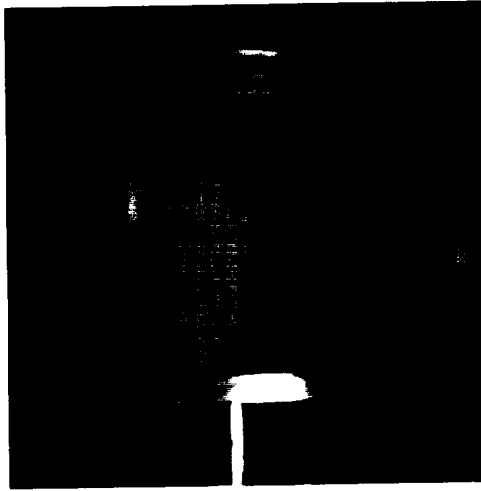


Figure 1. Aluminum/aluminum oxide target installed in the ion beam sputter deposition facility.

deposition, the ion beam is allowed to impinge on the metal-only portion of the target. As the deposition progresses, the cylindrical target is rotated under the beam thereby increasing the fraction of dielectric. At the end of deposition, the ion beam is impinging on the dielectric-only portion of the target. In practice, the deposition typically progresses in discrete steps. Given the geometry of the ion beam sputter deposition facility utilized in this work, eleven steps were used. In most cases, equal deposition time was spent at each step. In some cases, additional deposition time was spent on early steps to prepare metal-rich coatings or additional deposition time was spent on later steps to prepare oxide-rich coatings.

Samples were created from targets composed of aluminum/aluminum oxide, nickel/aluminum oxide, titanium/aluminum oxide, and platinum/aluminum oxide. All coatings were deposited on 2.54 cm diameter aluminum substrates, diamond turned to a mirror finish. The mirror finish was selected to help minimize emittance.

The optical performance of the solar selective coating was evaluated by measuring its reflectance in the wavelength range of 250 to 2500 nanometers utilizing a Perkin-Elmer Lambda-19 spectrophotometer equipped with a 15 cm diameter integrating sphere, and by measuring its reflectance in the wavelength range of 2 to 25 micrometers utilizing a Surface Optics Corporation SOC-400t portable infrared reflectometer. Solar absorptance was calculated by subtracting the reflectance at each wavelength in the wavelength range of 250 to 2500 nanometers from unity, and the resulting curve was weighted with respect to the air mass zero solar spectrum. Infrared emittance was calculated by subtracting the reflectance at each wavelength in the wavelength range of 2 to 25 micrometers from unity, and the resulting curve was weighted with respect to the black body curve for a given temperature, i.e. 25°C. Black body curves representing other temperatures could also be used in the calculation. In this approach, solar absorptance is independent of temperature and infrared emittance is dependent on temperature. The reflectance curves were combined and plotted on a logarithmic wavelength scale, for comparison.

Fused silica witness coupons present during sputter deposition were used to identify the thickness of each film using profilometry.

Results and Discussion

The ideal solar selective coating has the reflectance characteristics shown in Figure 2: a low reflectance in the visible spectral range, a high reflectance in the infrared spectral range, and a sharp transition in between. These reflectance characteristics yield in one surface the combined properties of high solar absorptance and low infrared emittance. For applications that will operate in the vicinity of 450°C, the sharp transition between the two extremes should occur near a wavelength of 2 micrometers. At lower operating temperatures, the sharp transition may occur at longer wavelengths. However, at higher operating temperatures, the sharp transition must occur at shorter wavelengths and with the drawback of reduced solar absorptance.

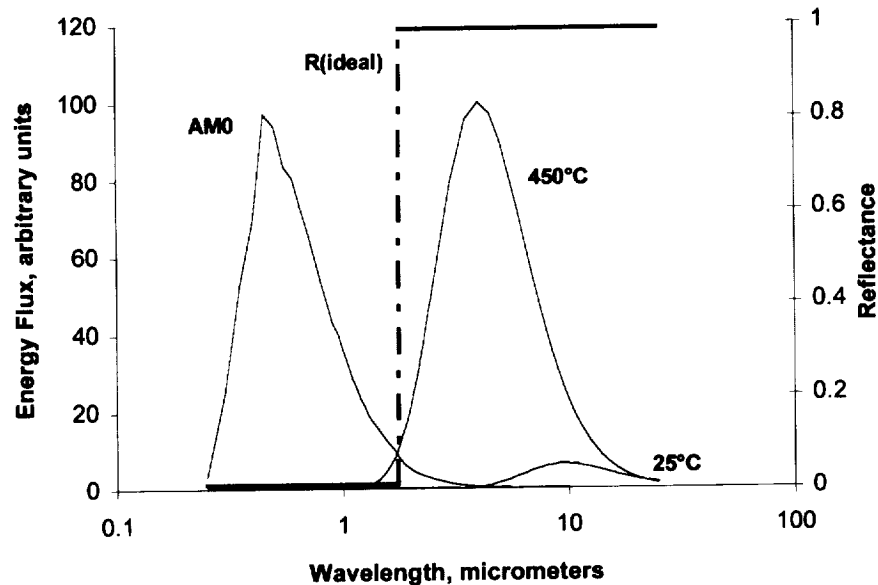


Figure 2. The air mass zero solar spectrum and blackbody curves for 25°C and 450°C.

In molecular mixtures of metal and dielectric, both the shape of the reflectance curve and the resulting α and ϵ values can vary with the chemical composition and the thickness of the coating.

Chemical Composition

The reflectance of four cermet coatings having four different chemical compositions is summarized in Figure 3. All four coatings were deposited by ion beam sputter deposition, and the change in their through thickness composition was created by the rotation and dwell time of their respective cylindrical target. Similar rotation and dwell time conditions were used for all four targets. Owing to differences in the sputtering of the target materials, thickness values varied: 3400 angstroms for the aluminum/aluminum oxide combination, 1800 angstroms for the nickel/aluminum oxide combination, 2400 angstroms for the titanium/aluminum oxide combination, and 5000 angstroms for the platinum/aluminum oxide combination. The titanium/aluminum oxide combination yielded the sharpest transition, with the transition occurring near the desired value of 2 micrometers. The nickel/aluminum oxide combination exhibited a less abrupt transition, at a value less than 2 micrometers.

Thickness

Deposition from each cylindrical target was controlled by rotation and dwell time. Given the great flexibility in selecting these parameters for ion beam sputter deposition from a cylindrical target, along with other parameters such as ionizing gas and beam current, many different deposition scenarios were tried and many different thin film mixtures were produced. The α and ϵ values for each metal/dielectric combination are presented here, in graphical form, as a function of coating thickness. By presenting the optical

properties data in this way, trade offs between α and ϵ as a function of coating thickness may be seen. A discussion of future work, including the need for high temperature durability testing, will follow.

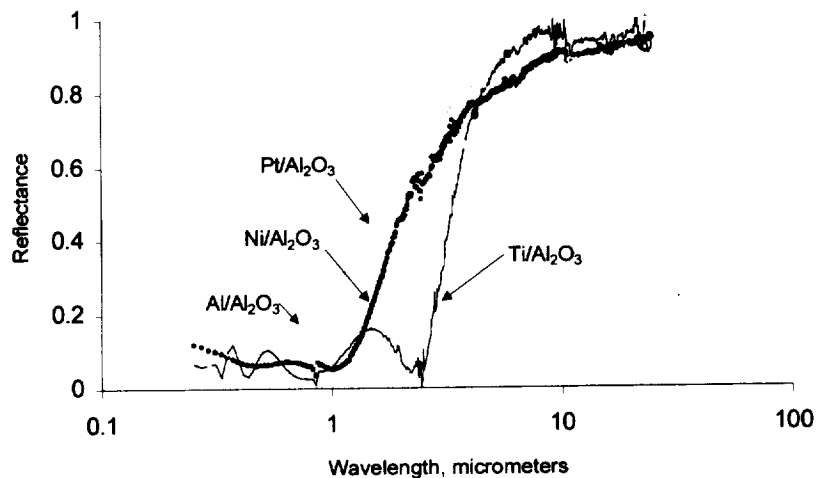


Figure 3. Reflectance as a function of wavelength for four molecular mixtures of metal and dielectric.

Figure 4 shows the α and $\epsilon_{25^\circ\text{C}}$ values for the aluminum/aluminum oxide combination of cermet coatings. As the coating thickness increases, α increases to its maximum at approximately 2500 angstroms and declines gradually thereafter. As the coating thickness increases, ϵ remains essentially constant until reaching 2000 angstroms and increases gradually thereafter. To utilize aluminum/aluminum oxide cermet coatings for applications where it is important to absorb solar energy, optimum performance would be

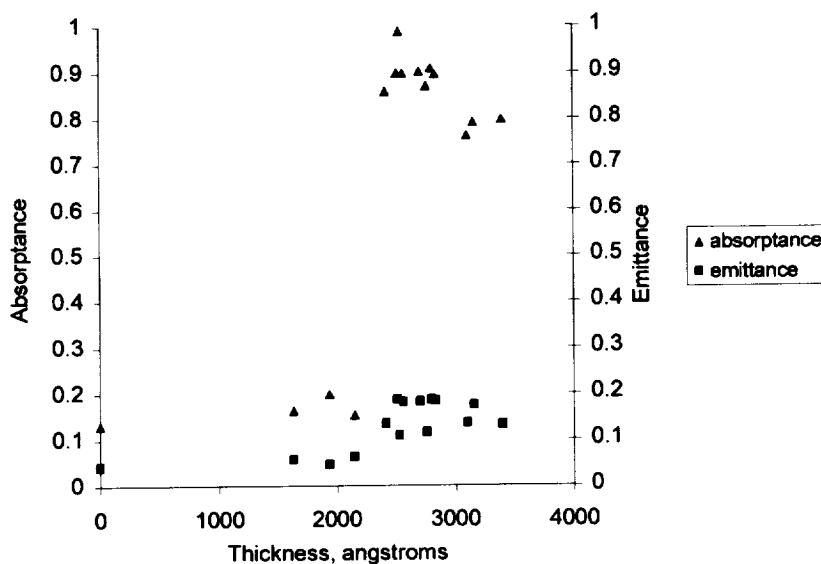


Figure 4. The α and $\epsilon_{25^\circ\text{C}}$ values of aluminum/aluminum oxide thin film mixtures.

achieved where α is high, in the vicinity of 2500 angstroms. However, there is a small penalty to pay in performance because ϵ has already started to increase at that thickness.

Figure 5 shows the α and ϵ values for the nickel/aluminum oxide combination of cermet coatings. As the coating thickness increases, α increases to its maximum at approximately 2200 angstroms. As the coating thickness increases, ϵ remains essentially constant over the limited range that was tested. To utilize

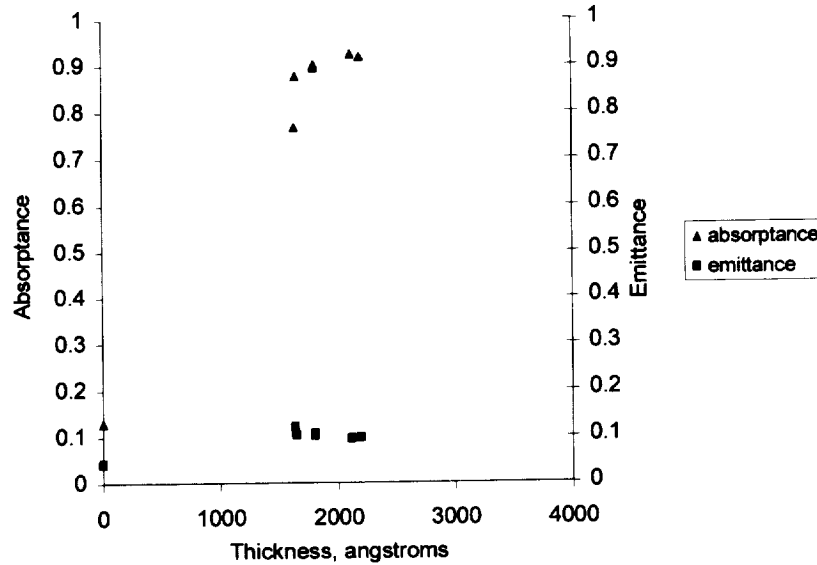


Figure 5. The α and $\epsilon_{25^\circ\text{C}}$ values of nickel/aluminum oxide thin film mixtures.

nickel/aluminum oxide cermet coatings for applications where it is important to absorb solar energy, optimum performance would be achieved where α is high and ϵ is low, in the vicinity of 2200 angstroms.

Figure 6 shows the α and ϵ values for the titanium/aluminum oxide combination of cermet coatings. In this case, as the coating thickness increases, α increases at thickness values of 1300 to 1900

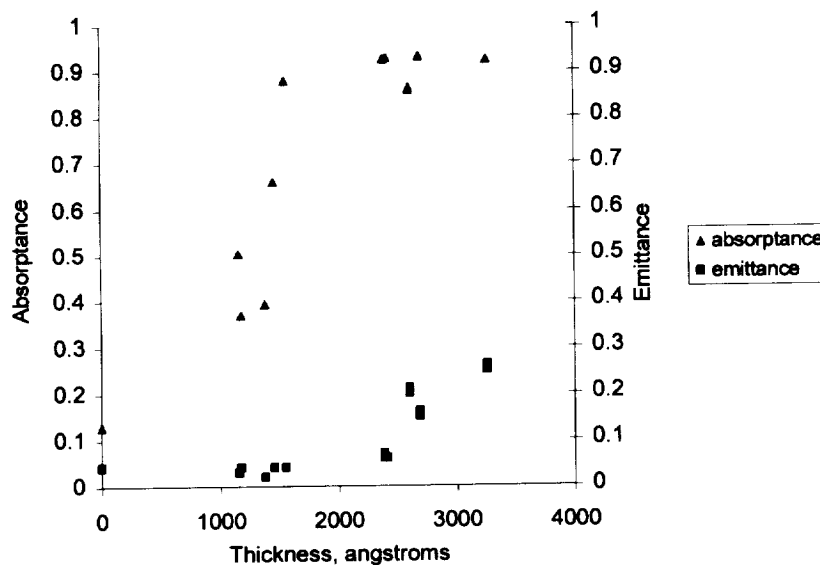


Figure 6. The α and $\epsilon_{25^\circ\text{C}}$ values of titanium/aluminum oxide cermet coatings.

angstroms, reaching its maximum at approximately 2500 angstroms. However, as the coating thickness increases, ϵ remains constant out to approximately 2200 angstroms and increases thereafter. Hence, optimum thermal performance of this cermet coating would occur in the vicinity of 2000 angstroms, with little to no penalty to pay in performance because ϵ remains low in this vicinity.

Additional work is underway utilizing the platinum/aluminum oxide cermet. The amount of platinum metal in the target is at a minimum and sputtering conditions are being chosen judiciously.

Future Work

Although this work has concentrated on utilizing several metals combined with one dielectric, additional work is needed to identify the optical performance of thin film molecular mixtures of combinations that utilize other dielectrics, such as silicon dioxide and aluminum nitride. Although high temperature performance of thin film molecular mixtures can be inferred from the high temperature characteristics of their constituents, additional work is needed to evaluate optical performance after heating. Future thermal modeling of potential hardware will need to consider the temperature dependence of the emittance. Additional work is also needed at the molecular level, to identify the mechanisms responsible for the observed optical properties. Auger profiling and x-ray photoelectron spectroscopy could be used to identify exact chemical composition as a function of thickness and shed some light on the types of chemical bonding that occur through the thickness of the coating. Finally, optical modeling is needed to help optimize current thin film molecular mixtures and to identify new candidate combinations for future cermet coatings.

Conclusions

Thin film molecular mixtures of metal and dielectric are being explored as candidates for solar selective coatings. The thin film molecular mixtures may be utilized to absorb solar energy at the heat inlet surface of a heat engine, or may be applied to the surface of a solar collector utilized to collect heat for a thermal bus application. The optical properties of four candidate thin film molecular mixtures were evaluated as a function of wavelength and as a function of film thickness. The four candidate coatings were sputter deposited molecular mixtures of aluminum and aluminum oxide, nickel and aluminum oxide, titanium and aluminum oxide, and platinum and aluminum oxide. Reflectance measurements indicated all four coatings exhibited the combined properties of high solar absorptance and low infrared emittance, to varying degrees, with the titanium and aluminum oxide combination having the best combined properties. Solar absorptance and infrared emittance summarized as a function of coating thickness revealed that the thin film mixtures must be at least 1800 to 2100 angstroms thick in order to provide adequate solar absorptance properties. However, care must be taken to avoid coatings that are too thick, yielding decreased optical performance at the expense of increased emittance.

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